JC14 Rec'd PCT/PTO 19 DEC 2001

Customized FORM PTO-1390 U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY DOCKET NO. P07472US00/WEJ

U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 10/018401

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/AU00/00696	20 JUNE 2000	22 JUNE 1999

TITLE OF INVENTION: EPITAXIAL FILMS

APPLICANT(S) FOR DO/EO/US: TRANS, Nguyen et al.

Applicant herewith submits to the US Designated/Elected Office (DO/EO/US) the following items and other information:

- [x] 1. This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
- [ ] 2. This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 USC 371.
- [x] 3. This express request to begin national examination procedures (35 USC 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 USC 371(b) and PCT Art. 22 and 39(1).
- [x] 4. A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
- [x] 5. A **copy** of the International Application as filed (35 U.S.C. 371 (c)(2))
  - [ ] a. is transmitted herewith (required only if not transmitted by the International Bureau).
  - [x] b. has been transmitted by the International Bureau.
  - [ ] c. is not required, as the application was filed in the United States Receiving Office (RO/US).
- [ ] 6. A **translation** of the International Application into English (35 U.S.C. 371(c)(2)).
- [x] 7. Amendments to the claims of the International Appln. under PCT Article 19 (35 USC 371 (c)(3))
  - [ ] a. are transmitted herewith (required only if not transmitted by the International Bureau).
  - [ ] b. have been transmitted by the International Bureau.
  - [ ] c. have not been made; however, the time limit for making such amendments had NOT expired.
  - [x] d. have not been made and will not be made.
- [ ] 8. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
- [ ] 9. An **oath** or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
- [ ] 10. A translation of the annexes to the Int'l Prelim. Exam. Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 20. below concern document(s) or information included:

- [ ] 11. An **Information Disclosure Statement** under 37 C.F.R. 1.97 and 1.98.
- [ ] 12. An **Assignment** document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
- [x] 13. A **First preliminary amendment.**
- [ ] 14. A Second or Subsequent preliminary amendment.
- [ ] 15. A substitute specification.
- [ ] 16. A change of power of attorney and/or address letter.
- [ ] 17. A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 & 35 USC 1.821-825.
- [ ] 18. A second copy of the published international application under 35 USC 154(d)(4).
- [ ] 19. A second copy of the English translation of the international application under 35 USC 154(d)(4).
- [ ] 20. Other items or information:
  - [ ]
  - [ ]

- [ ] A copy of the Notification of Missing Requirements under 35 U.S.C. 371.
- [ ] In the event that a petition for extension of time is required to be submitted herewith, and in the event that a separate petition does not accompany this response, applicant hereby petitions under 37 CFR 1.136(a) for an extension of time of as many months as are required to render this submission timely. Any fee is authorized in 17(c).

Date: 19 December 2001

JC13 Rec'd PCT/PTO 19 DEC 2001

U.S. APPLICATION NO. (If known) 10/018401	INTERNATIONAL APPLICATION NO. PCT/AU00/00696	ATTORNEY DOCKET NO. P07472US00/WEJ

☒ 21. **The following fees are submitted:**

☒ **Basic National Fee** (37 CFR 1.492 (a) (1)-(5):

			CALCULATIONS	PTO USE ONLY
☒ Neither Int'l Prelim. Exam. fee nor Int'l Search fee paid to USPTO		$1040		
☐ Search Report has been prepared by the EPO or JPO		$ 890		
☐ No Int'l Prelim. Ex. fee paid to USPTO but Int'l Search fee paid to USPTO		$ 740		
☐ International preliminary examination fee paid to USPTPO		$ 710		
☐ Int'l Prelim. Ex. fee paid to USPTO & all claims satisfied PCT Art. 33(1)-(4)		$ 100		
ENTER APPROPRIATE BASIC FEE AMOUNT =			$ 1040	
☐ Surcharge of **$130** for furnishing the oath or declaration later than from the earliest claimed priority date (37 CFR 1.492(e)).	☐ 20 mos. ☐ 30 mos.	+	$	

CLAIMS	*NUMBER FILED*	*NUMBER EXTRA*	*RATE*		
Total Claims	17 - 20 =		X **$18** =	$	
Independent Claims	03 - 03 =		X **$84** =	$	
☐ Multiple Dependent Claim(s) (if applicable)			+ **$280** =	$	
TOTAL OF ABOVE CALCULATIONS =				$ 1040	
☒ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by ½.			-	$ 520	
SUBTOTAL =				$ 520	
☐ Processing fee of **$130** for furnishing the **English translation** later than from the earliest claimed priority date (37 CFR 1.492(f)).		☐ 20 mos. ☐ 30 mos.	+	$	
TOTAL NATIONAL FEE =				$ 520	
☐ Fee for recording the enclosed **assignment** (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40** per property			+	$	
TOTAL FEES ENCLOSED =				$ 520	
			Amount to be	*Refunded*	$
				Charged	$

☒ a. A **check** in the amount of $ 520 to cover the above fees is enclosed.

☐ b. Please charge my Deposit Account No. 12-0555 in the amount of $ to cover the above fees.

☒ c. The Commissioner is hereby authorized to charge any additional fees required or credit overpayment to Deposit Account No. 12-0555.

Note: *Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.*

SEND ALL CORRESPONDENCE TO:	
WILLIAM E. JACKSON	SIGNATURE: Douglas E. Jackson
At the address (below) of **CUSTOMER NO. 00881.**	NAME: Douglas E. Jackson
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ALEXANDRIA, VA 22314	Date: 19 December 2001

10/018401

JC13 Rec'd PCT/PTO 19 DEC 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent

In re patent application of: TRAN et al.

Serial No.: NEW APPLICATION

Filed: On even date herewith

For: EPITAXIAL FILM

Examiner:

Art Unit:

Dckt No.: P07472US00/WEJ

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C.

S I R:

Prior to examination, please amend the above-identified application as follows.

IN THE CLAIMS:

A clean version of the amended claims is provided herewith in **Attachment A**. It will be noted that claims 1, 3, 4, 8 and 10-17 have been amended relative to the previously provided version as shown by the marked up version thereof in **Attachment B** provided herewith.

REMARKS

By this Amendment, the claims have been rewritten to reduce the multiple dependencies.

Further and favorable action is solicited.

Respectfully submitted,

Date: 12/19/01

By: [signature]
Douglas E. Jackson
Registration No. 28518

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ATTACHMENT A

Clean Replacement/New Claims (entire set of pending claims)

Following herewith is a clean copy of the entire set of pending claims.

1. (amended) An epitaxial zinc-based II-VI semiconductor film grown using single source chemical vapor deposition.

2. An epitaxial film as claimed in claim 1, wherein the epitaxial film comprises ZnS.

3. (amended) An epitaxial film as claimed in claim 2, wherein the ZnS is grown using zinc diethyldithiocarbamate as precursor for the single source chemical vapor deposition.

4. (amended) An epitaxial film as claimed in claim 2, wherein the ZnS is grown using $Zn(S_2CRN_2)_2$, where R comprises an alkyl group, as a precursor for the single source chemical vapor deposition.

5. A process as claimed in claim 4, wherein the number of carbon atoms in the alkyl group is in the range from 1 to 6.

6. A process comprising the steps of utilizing single source chemical vapor deposition for growing epitaxial zinc-based II-VI semiconductor film on a substrate.

7. A process as claimed in claim 6, wherein the epitaxial film comprises ZnS.

8. (amended) A process as claimed in claim 7, wherein the process comprises the use of $Zn(S_2CNR_2)_2$, where R comprises an alkyl group, as precursor for the single source chemical vapor deposition.

9. A process as claimed in claim 8, wherein the number of carbon atoms in the alkyl group is in the range from 1 to 6.

10. (amended) A process as claimed in claim 7, wherein the process comprises the use of zinc diethyldithiocarbamate as a precursor for the single source chemical vapor deposition.

11. (amended) A process as claimed in claim 6, wherein the substrate comprises a silicon substrate.

12. (amended) A substrate coated with a coating comprising an eptiaxial zinc-based II-VI semiconductor film grown using single source chemical vapor deposition.

13. (amended) A substrate as claimed in claim 12, wherein the substrate comprises silicon.

14. (amended) A substrate as claimed in claim 12, wherein the epitaxial film comprises ZnS.

15. (amended) A process for growing an eptiaxail zinc-based II-VI semiconductor film, the process comprising the steps of:

- cleaning a substrate,
- heating the substrate to a deposition temperature,
- the sublimation of a single source chemical vapor deposition precursor;
- the pyrolysis of the precursor molecules on the heated substrate; and
- the formation of the epitaxial film on the heat substrate.

16. (amended) A process as claimed in claim 15, wherein the substrate comprises silicon.

17. (amended) A process as claimed in claim 15, wherein the epitaxial film comprises ZnS.

ATTACHMENT B

Marked Up Replacement Claims

Following herewith is a marked up copy of each rewritten claim together with all other pending claims.

1. (amended) An epitaxial zinc-based II-VI semiconductor film grown using single source chemical ~~vapour~~vapor deposition.

2. An epitaxial film as claimed in claim 1, wherein the epitaxial film comprises ZnS.

3. (amended) An epitaxial film as claimed in claim 2, wherein the ZnS is grown using zinc diethyldithiocarbamate as precursor for the single source chemical ~~vapour~~vapor deposition.

4. (amended) An epitaxial film as claimed in claim 2, wherein the ZnS is grown using $Zn(S_2CRN_2)_2$, where R comprises an alkyl group, as a precursor for the single source chemical ~~vapour~~vapor deposition.

5. A process as claimed in claim 4, wherein the number of carbon atoms in the alkyl group is in the range from 1 to 6.

6. A process comprising the steps of ~~utilising~~utilizing single source chemical ~~vapour~~vapor deposition for growing epitaxial zinc-based II-VI semiconductor film on a substrate.

7. A process as claimed in claim 6, wherein the epitaxial film comprises ZnS.

8. (amended) A process as claimed in claim 7, wherein the process comprises the use of $Zn(S_2CNR_2)_2$, where R comprises an alkyl group, as precursor for the single source chemical ~~vapour~~vapor deposition.

9. A process as claimed in claim 8, wherein the number of carbon atoms in the alkyl group is in the range from 1 to 6.

10. (amended) A process as claimed in claim 7, wherein the process comprises the use of zinc diethyldithiocarbamate as a precursor for the single source chemical ~~vapour~~vapor deposition.

11. (amended) A process as claimed in ~~any one of claims 6 to 10~~claim 6, wherein the substrate comprises a silicon ~~(111)~~ substrate.

12. (amended) A substrate coated with a coating comprising an eptiaxial zinc-based II-VI semiconductor film grown using single source chemical ~~vapour~~vapor deposition.

13. (amended) A substrate as claimed in claim 12, wherein the substrate comprises silicon ~~(111)~~.

14. (amended) A substrate as claimed in claim~~s~~ 12 ~~to 13~~, wherein the epitaxial film comprises ZnS.

15. (amended) A process for growing an eptiaxail zinc-based II-VI semiconductor film, the process comprising the steps of:

- cleaning a substrate,
- heating the substrate to a deposition temperature,
- the sublimation of a single source chemical ~~vapour~~vapor deposition precursor;
- the pyrolysis of the precursor molecules on the heated substrate; and
- the formation of the epitaxial film on the heated substrate.

16. (amended) A process as claimed in claim 15, wherein the substrate comprises silicon ~~(111)~~.

17. (amended) A process as claimed in claim 15 ~~or 16~~, wherein the epitaxial film comprises ZnS.

Rec'd PCT/PTO 10 APR 2002

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent

In re patent application of: TRAN et al.

Serial No.: 10/018,401

Filed: December 19, 2001

For: EPITAXIAL FILM

Examiner:

Art Unit:

Dckt No.: P07472US00/WEJ

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C.

S I R:

Prior to examination, please amend the above-identified application as follows.

IN THE CLAIMS:

A clean version of the all pending claims is provided herewith in **Attachment A**. It will be noted that claims 13 and 16 have been amended relative to the previously provided version as shown by the marked up version thereof in **Attachment B** provided herewith.

REMARKS

By this Amendment, the claims have been amended to correct errors in the previous Preliminary Amendment.

Further and favorable action is solicited.

Respectfully submitted,

Date: April 10, 2002

By: William E. Jackson
William E. Jackson
Registration No. 24,016

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ATTACHMENT A

Clean Replacement/New Claims

Following herewith is a clean copy of the amended claims.

13. (Thrice Amended) A substrate as claimed in claim 12, wherein the substrate comprises silicon (111).

16. (Thrice Amended) A process as claimed in claim 15, wherein the substrate comprises silicon (111).

ATTACHMENT B

Marked Up Replacement Claims

Following herewith is a marked up copy of each rewritten claim.

13. (Thrice Amended) A substrate as claimed in claim 12, wherein the substrate comprises ~~(111)~~ silicon (111).

16. (Thrice Amended) A process as claimed in claim 15, wherein the substrate comprises ~~(111)~~ silicon (111).

Rec'd PCT/PTO 19 DEC 2001

10/018401

EPITAXIAL FILMS

Field of the Invention

The present invention relates broadly to the growth of epitaxial II-VI semiconductor films. The invention will be described herein with reference to the growth of epitaxial zinc sulfide (ZnS) on silicon (Si) (111) substrates, but it will be appreciated that the invention does have broader applications relating to growth of epitaxial II-VI semiconductor films of different materials and/or on different substrates.

Background of the Invention

Films that grow with singular crystallographic orientation in all directions are referred to as epitaxial films. This has to be contrasted with poly-crystalline thin films, which include a large number of crystallites — but with variable orientations with respect to each other.

Epitaxial thin films have been produced using a variety of different techniques, including molecular beam epitaxy (MBE), vapour phase epitaxy (VPE) and atomic layer epitaxy (ALE). However, a common characteristic of those techniques is that the epitaxial film growth requires multiple sources for the film elements, for example separate sources for zinc (Zn) and sulphur (S) are required for the epitaxial growth of ZnS films. Therefore, such techniques can have the disadvantage of being rather complex processes, during which a large number of variables must be controlled. This often results in high costs associated with the operation of machines for epitaxial film growth.

Epitaxial thin films are desirable for a large number of applications including light emitting layers for diodes, as active layers in optical/electro-optical thin film devices and as coatings. In this application, the single-crystal like characteristics of epitaxial films are utilised, which are typically superior to the characteristics of polycrystalline films.

Summary of the Invention

In accordance with a first aspect of the present invention there is provided an epitaxial zinc-based II-VI semiconductor film grown using single source chemical vapour deposition.

In one embodiment, the epitaxial film comprises ZnS.

Preferably, the ZnS is grown using zinc diethyldithiocarbamate as precursor for the single source chemical vapour deposition.

In another preferred embodiment, the ZnS is grown using $Zn(S_2CNR_2)_2$, where R comprises an alkyl group, as a precursor for the single source chemical vapour deposition.

The number of carbon atoms in the alkyl group is preferably in the range from 1 to 6.

In accordance with a second aspect of the present invention there is provided a process comprising the steps of utilising single source chemical vapour deposition for growing an epitaxial zinc-based II-VI semiconductor film on a substrate.

In one embodiment, the epitaxial film comprises ZnS.

In one preferred embodiment the process comprises the use of zinc diethyldithiocarbamate as a precursor for the single source chemical vapour deposition.

In another preferred embodiment, the ZnS is grown using $Nz(S_2CNR_2)_2$, where R comprises an alkyl group, as a precursor for the single source chemical vapour deposition.

The number of carbon atoms in the alkyl group is preferably in the range from 1 to 6.

Preferably, the substrate comprises a silicon (111) substrate.

In accordance with a third aspect of the present invention, there is provided a substrate coated with a coating comprising an epitaxial zinc-based II-VI semiconductor film grown using single source chemical vapour deposition.

Preferably, the substrate comprises silicon (111).

In one embodiment, the epitaxial film comprises ZnS.

In accordance with a fourth aspect of the present invention, there is provided a process for growing an epitaxial zinc-based II-VI semiconductor film, the process comprising the steps of cleaning a substrate, heating the substrate to a deposition temperature, the sublimation of a single source chemical vapour deposition precursor;

the pyrolysis of the precursor molecules on the heated substrate; and

the formation of the epitaxial film on the heated substrate.

Preferably, the substrate comprises silicon (111).

In one embodiment, the epitaxial film comprises ZnS. Preferred forms of the invention will now be described, by way of example only, with reference to the accompanying drawings.

Brief Description of the Drawings

Figure 1 is a schematic drawing of a deposition chamber embodying the present invention.

Figure 2 shows angle dependent X-ray photoelectron defraction measurements of epitaxial films embodying the present invention.

Figure 3 is schematic drawing illustrating a side view of a ZnS crystalline structure.

Figure 4 shows an X-ray photoelectron spectroscopy wide scan of a ZnS film embodying the present invention.

Figure 5 shows an angle dependent X-ray photoelectron defraction measurements of a ZnS film after sputtering.

Figure 6 shows energy dependent X-ray photoelectron defraction measurements of an epitaxial film embodying the present invention.

Figure 7 is schematic drawing illustrating a side view of a ZnS crystalline structure.

Figure 8 is a schematic drawing illustrating the formation of an epitaxial film embodying the present invention.

Figure 9 is a block diagram illustrating the growth of epitaxial films embodying the present invention.

Figure 10 is a schematic diagram illustrating a device application embodying the present invention.

Detailed Description of the Preferred Embodiments

In Figure 1, a high vacuum deposition chamber 10 (base pressure 10^{-7} Torr) comprises a resistively heated Knudsen cell 12 loaded with a zinc diethyldithiocarbamate precursor powder (not shown) for the single source chemical vapour deposition (SSCVD). A silicon Si(111) substrate 19 is mounted on a sample holder 16 on a heater 100 and the epitaxial film (not shown) is formed on the substrate 19. The chamber 10 further comprises a view port 11, a port 13 to which a vacuum pump (not shown) is connected and a flexible flange 15 as part of a x,y,z manipulator 17 for the heater 100.

As illustrated in Figure 8, sublimed zinc diethyldithiocarbamate molecules 80 impinge on the heated substrate 19. In the diethyldithiocarbamate molecules 80, the zinc atom is in a similar environment to that of zinc in crystalline ZnS. The SSCVD growth of the ZnS epitaxial film 84 proceeds via the pyrolysis of $Zn[S_2CN(C_2H_5)_2]_2$ on the heated substrate 19 (400ºC):

$$Zn[S_2CN(C_2H_5)_2]_2 \rightarrow ZnS + C_2H_5NCS + (C_2H_5)_3NCS_2 \qquad (1)$$

C_2H_5NCS and $(C_2H_5)_3NCS_2$ decompose into by-products such as C_2H_4, CS_2 and $(C_2H_5)NH$ which are volatile in vacuum and therefore do not remain on the heated substrate 19 during the ZnS epitaxial film growth.

In this embodiment epitaxial film growth of ZnS was found on the Si (111) surface (lattice mismatch ~0.2%).

As shown in Figure 9, in one embodiment the growth of epitaxial films comprises the cleaning of the Si substrate (step 90), the heating of the Si substrate (step 92), the sublimation of the diethyldithiocarbamate precursor (step

94), the pyrolysis of the diethyldithiocarbamate molecules on the heated substrate (step 96) and the formation of the epitaxial ZnS film on the heated substrate (step 98).

The cleaning of the Si(111) substrates (step 90) in one embodiment comprises the sequence of steps outlined in Table 1.

1	annealing in oxygen	1050ºC	30 min
2	rinse in deionised H_2O	room temp (ultrasonic bath)	5 min
3	rinse in EtOH	room temp (ultrasonic bath)	5 min
4	rinse in Iso-propyl alcohol	room temp (ultrasonic bath)	5 min
5	N_2 blown dry		30 sec
6	$12H_2O$: $7NHF_4$: 1HF	room temp	10 min
7	rinse in deionised H_2O	room temp	1 min
8	N_2 blown dry		30 sec
9	$5H_2O$: 1HCl : $1H_2O_2$	80ºC, oil bath	10 min
10	rinse in deionised H_2O	room temp	1 min
11	N_2 blown dry		30 sec
12	$12H_2O$: $7NHF_4$: 1HF	room temp	10 min
13	rinse in deionised H_2O	room temp	1 min
14	N_2 blown dry		30 sec
15	$5H_2O$: 1HCl : $1H_2O_2$	80ºC, oil bath	10 min
16	rinse in deionised H_2O	room temp	1 min
17	N_2 blown dry		30 sec
18	$12H_2O$: $7NHF_4$: 1HF	room temp	10 min
19	rinse in deionised H_2O	room temp	1 min
20	N_2 blown dry		30 sec
21	$5H_2O$: 1HCl : $1H_2O_2$	80ºC, oil bath	10 min
22	rinse in deionised H_2O	room temp	1 min
23	N_2 blown dry		30 sec
24	NH_4F (40%) or HF (5%)	room temp	10 min

25	rinse in absolute EtOH	room temp	2 min
26	Mounting onto sample holder/heater 16		
27	loading into deposition chamber 10		
28	heating for removing surface contaminants	350ºC, vacuum (10^{-8} torr)	15 min

In will be appreciated, however, that other cleaning step sequences and different treatment times may be applied, which may e.g. comprise sputtering and annealing steps in the high vacuum deposition chamber 10 (Figure 1).

<u>Film Characterisation</u>

The resulting epitaxial films were characterised using X-ray photoelectron spectroscopy (XPS) and X-ray photoelectron diffraction (XPD).

Figure 2 shows an angle dependent XPD scan of the Zn $2p_{3/2}$ intensity distribution for ZnS epitaxial films at thicknesses ranging from ~5 to 2000Å. The film thicknesses were estimated using the intensity attenuating of the XPS Si substrate peaks. The XPD measurements were performed after subsequent SSCVD deposition cycles.

The XPD patterns exhibit an intense and broad peaks 20, 22, and 24 at θ=0º which are the result of forward-scattering of Zn $2p_{3/2}$ photoelectrons by neighbouring atoms. In ZnS, every zinc atom is surrounded by four sulfur atoms in a tetrahedral arrangement which results in either a cubic (sphalerite) or a, slightly distorted, hexagonal (wurtzite) structure.

The enhanced XPD intensities 20, 22, 24 at θ=0º in curves a, b, and c of Figure 2 respectively therefore indicate that the film molecules have preferred orientation at the film-to-substrate interface and the Zn $2p_{3/2}$ photoelectrons are scattered by the sulfur neighbours perpendicular to the substrate.

As illustrated in Figure 3, the forward scattering enhancement 20, 22, 24 at θ=0º in curves a, b and c of Figure 2 is likely the result of forward-scattering of $Zn2p_{3/2}$ photoelectrons emitted from the zinc atoms 30 at the sulphur atoms 32, which are positioned directly above the zinc atoms 30 at a distance of 2.3 Å in an ideal ZnS cubic crystal structure.

In Figure 4, a XPS wide scan 40 for a typical ZnS epitaxial film embodying the present invention is shown. In the curve 40 shown in Figure 4, the silicon substrate peaks can also be observed, which are not fully attenuated due to the thinness of the ZnS epitaxial film on which the XPS measurement shown in Figure 4 was performed. The chemical composition obtained from XPS scans such as the one shown in Figure 4 were in agreement with those obtained for a ZnS reference sample.

In Figure 5, the curve 50 shows the XPD measurement for the 2000Å thick film of curve c of Figure 2 after Ar^+ ion etching.

During the Ar^+ ion etching, highly energetic (2000 electron Volt (2keV)) impact on the film surface, resulting in a disordering of the crystallographic structure of the surface. In curve 50 of Figure 5, the XPD scan therefore does not indicate a significant forward scattering enhancement at θ=0º.

Energy dependent XPD was employed to probe the in-plane orientation of the film molecules. The sample position and angle remained unchanged while the energy of the incoming X-rays was varied.

The energy dependent XPD features shown in Figure 6 are a result of diffraction of S 2p photoelectrons in the ZnS atomic network. The photoelectron take-off angle was 19º with respect to the surface plane, i.e. the measurement was sensitive for crystallographic order within the plane of the substrate. As diffraction is a long range order process (diffraction of photoelectrons requires single crystalline surfaces) the observation of peaks 60, 62, 64 demonstrates that the film is of epitaxial quality.

As illustrated in Figure 7, the peaks 60, 62, 64 in the measurement shown in Figure 6 are due to the forward scattering of S 2p photoelectrons emitted from the sulphur atoms 70 at zinc atoms 72, which are the next neighbours of the sulphur atoms 70 in the $[11\bar{1}]$ crystallographic direction 74, along which the measurement shown in Figure 6 was measured. The distance between the sulfur atoms 60 and the Zn atoms 72 in an ideal ZnS cubic crystal structure is 2.3 Å.

In the following, a specific device application embodying the present invention will be described with reference to Figure 10.

Silicon is transparent at the typical telecommunications wavelength and it has been shown that Silicon-On-Insulator (SOI) structures can be used as waveguides. In these structures the wave is guided by a thin silicon layer on SiO_2.

Figure 10 illustrates the principles of an optical modulator design 100. The silicon 102 is partially replaced by an epitaxial ZnS layer 104 which acts as waveguide. A suitable AC voltage applied across the ZnS layer 104 alters the refractive index of the ZnS and it is therefore possible to modulate light 105 guided through the film directly.

The epitaxial ZnS layer 104 is grown on the remaining slightly doped (111) oriented silicon layers 106 which also comprises the bottom electrode. A thin metal film 108

(e.g. Cr) is deposited onto the ZnS film 104 and form the top electrode. Optical losses are dependent on the density of defects in the ZnS layer 104 and it is therefore of significant advantage that they can be grown single crystalline using the technology of the present invention.

It will be appreciated by a person skilled in the art that the present invention is not limited to that specific application, but other applications are possible, including for example in other optical modulator devices, optical waveguide devices, transistor and diode devices, blue light emitting devices, solar cells, and as coatings for infrared sensing, emitting, or transmitting devices.

In the claims that follow and in the summary of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprising" is used in the sense of "including", i.e. the features specified may be associated with further features in various embodiments of the invention.

In the claims that follow and in the summary of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprising" is used in the sense of "including", i.e. the features specified may be associated with further features in various embodiments of the invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. An epitaxial zinc-based II-VI semiconductor film grown using single source chemical vapour deposition.

2. An epitaxial film as claimed in claim 1, wherein the epitaxial film comprises ZnS.

3. An epitaxial film as claimed in claim 2, wherein the ZnS is grown using zinc diethyldithiocarbamate as precursor for the single source chemical vapour deposition.

4. An epitaxial film as claimed in claim 2, wherein the ZnS is grown using $Zn(S_2CNR_2)_2$, where R comprises an alkyl group, as a precursor for the single source chemical vapour deposition.

5. A process as claimed in claim 4, wherein the number of carbon atoms in the alkyl group is in the range from 1 to 6.

6. A process comprising the steps of utilising single source chemical vapour deposition for growing an epitaxial zinc-based II-VI semiconductor film on a substrate.

7. A process as claimed in claim 6, wherein the epitaxial film comprises ZnS.

8. A process as claimed in claim 7, wherein the process comprises the use of $Zn(S_2CNR_2)_2$, where R comprises an alkyl group, as a precursor for the single source chemical vapour deposition.

9. A process as claimed in claim 8, wherein the number of carbon atoms in the alkyl group is in the range from 1 to 6.

10. A process as claimed in claim 7, wherein the process comprises the use of zinc diethyldithiocarbamate as a precursor for the single source chemical vapour deposition.

11. A process as claimed in any one of claims 6 to 10, wherein the substrate comprises a silicon (111) substrate.

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12. A substrate coated with a coating comprising an epitaxial zinc-based II-VI semiconductor film grown using single source chemical vapour deposition.

13. A substrate as claimed in claim 12, wherein the substrate comprises silicon (111).

14. A substrate as claimed in claims 12 or 13, wherein the epitaxial film comprises ZnS.

15. A process for growing an epitaxial zinc-based II-VI semiconductor film, the process comprising the steps of:

- cleaning a substrate,
- heating the substrate to a deposition temperature,
- the sublimation of a single source chemical vapour deposition precursor;
- the pyrolysis of the precursor molecules on the heated substrate; and
- the formation of the epitaxial film on the heated substrate.

16. A process as claimed in claim 15, wherein the substrate comprises silicon (111).

17. A process as claimed in claim 15 or 16, wherein the epitaxial film comprises ZnS.

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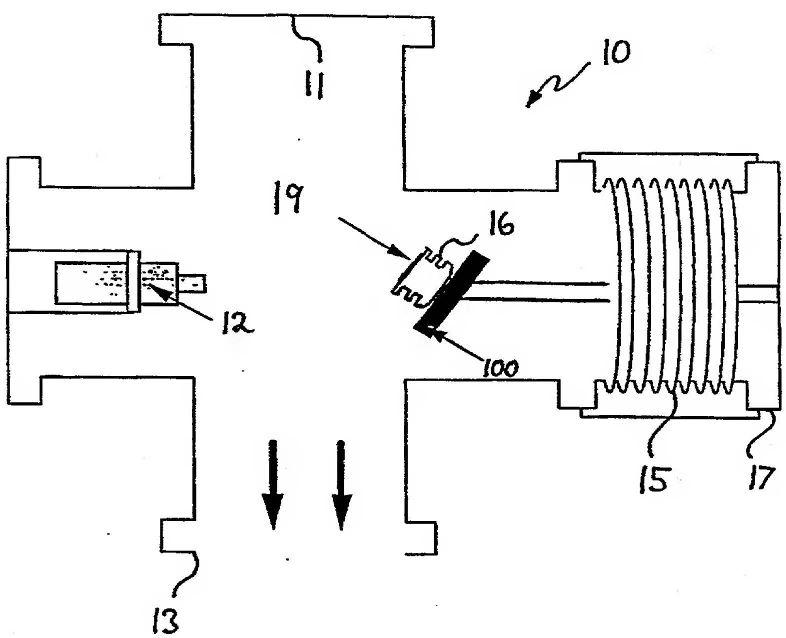

(57) Abstract: Growth of epitaxial zinc sulphide semiconductor film using zinc diethyldithiocarbamate precursor as single source.

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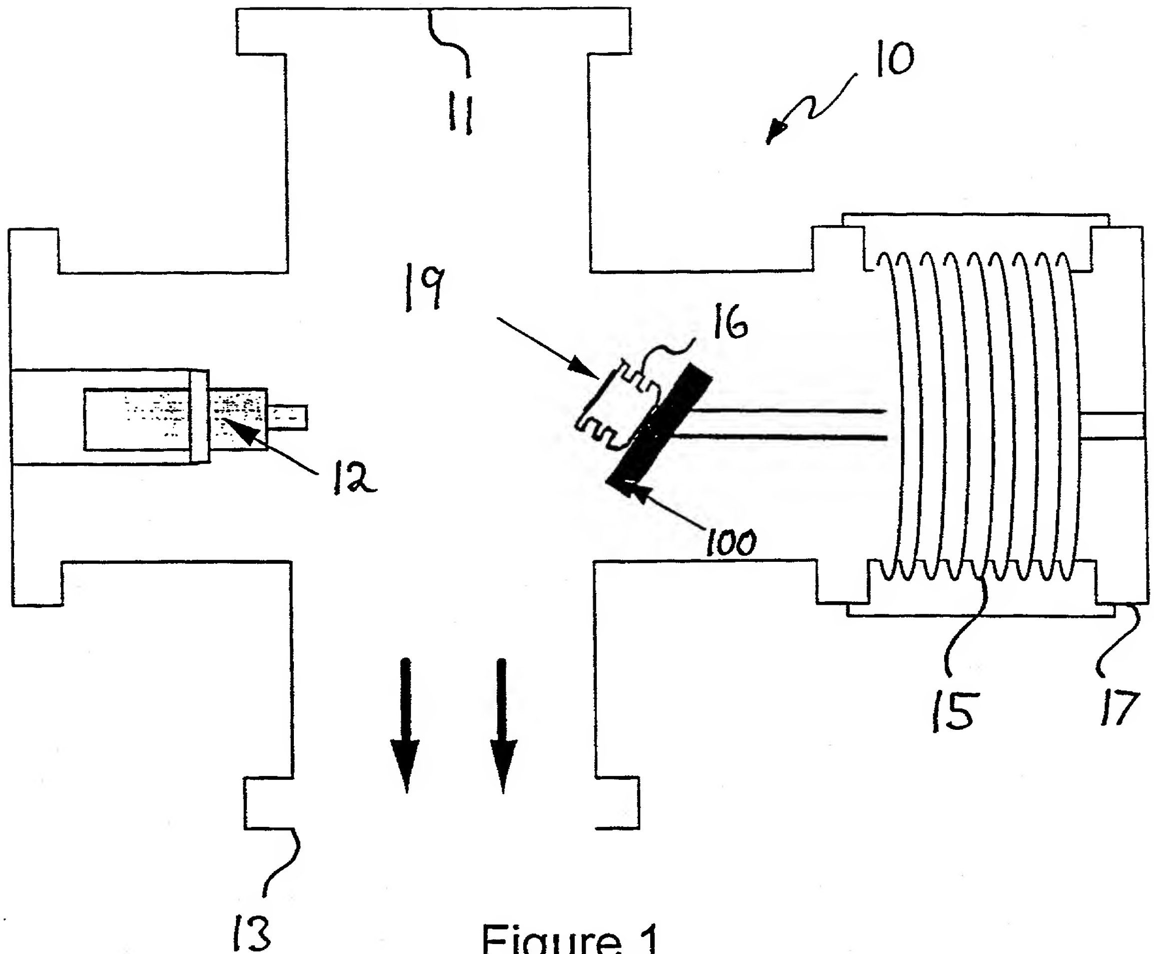

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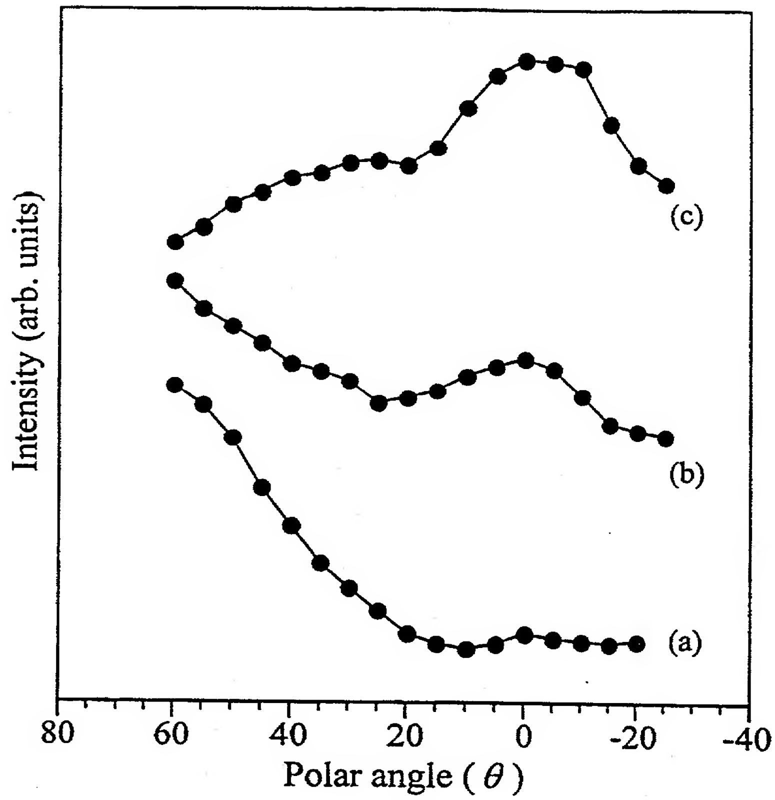

Figure 2

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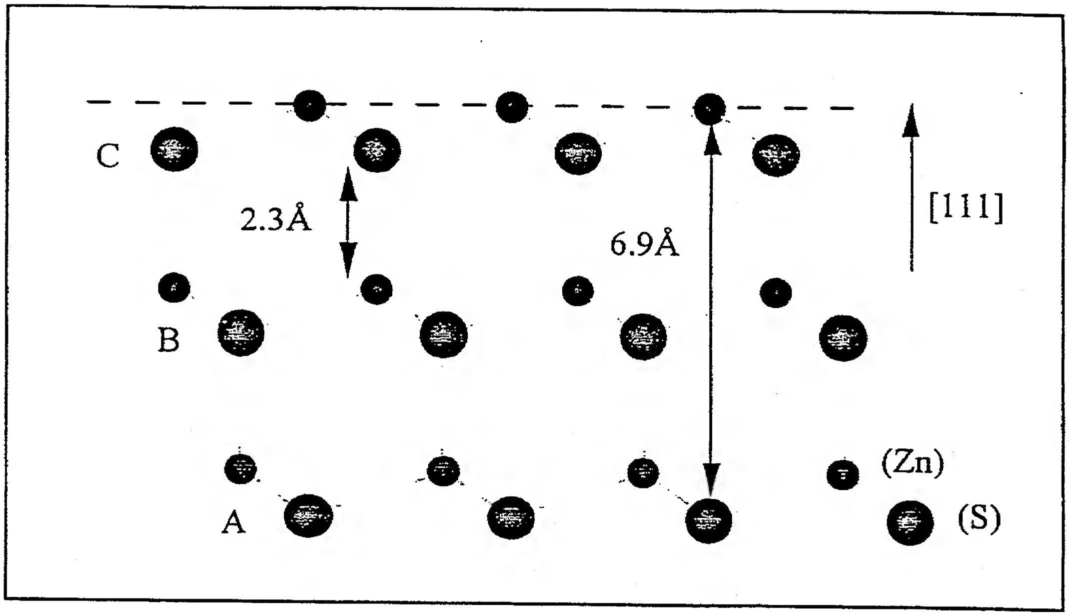

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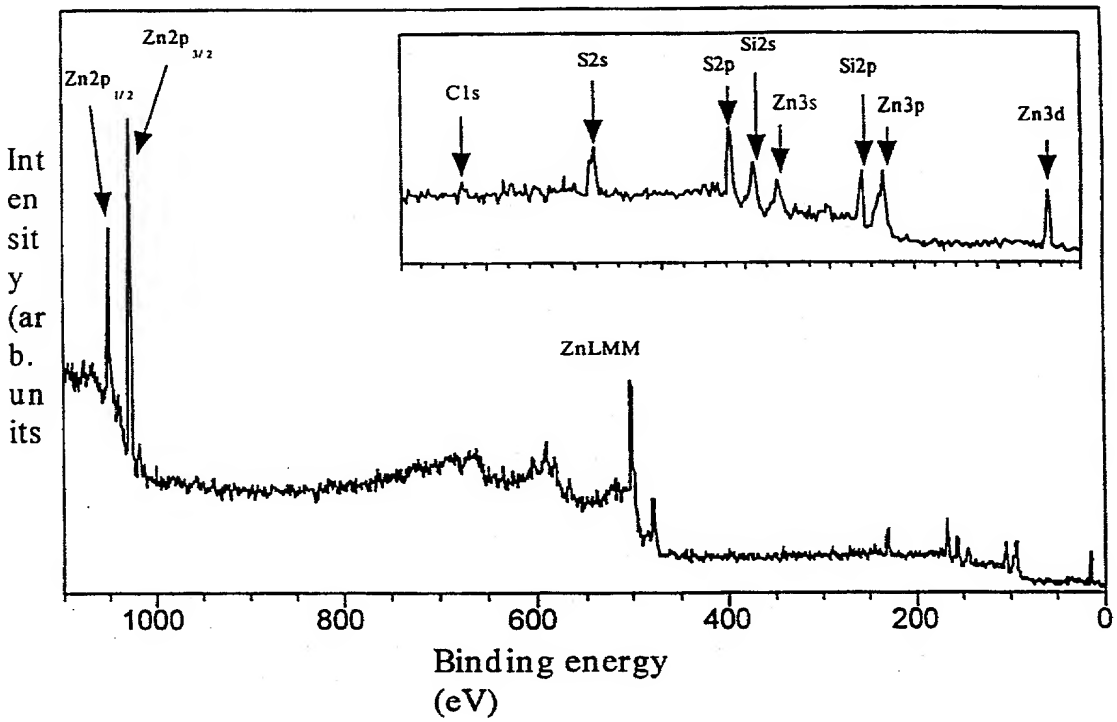
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C1s
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S2p
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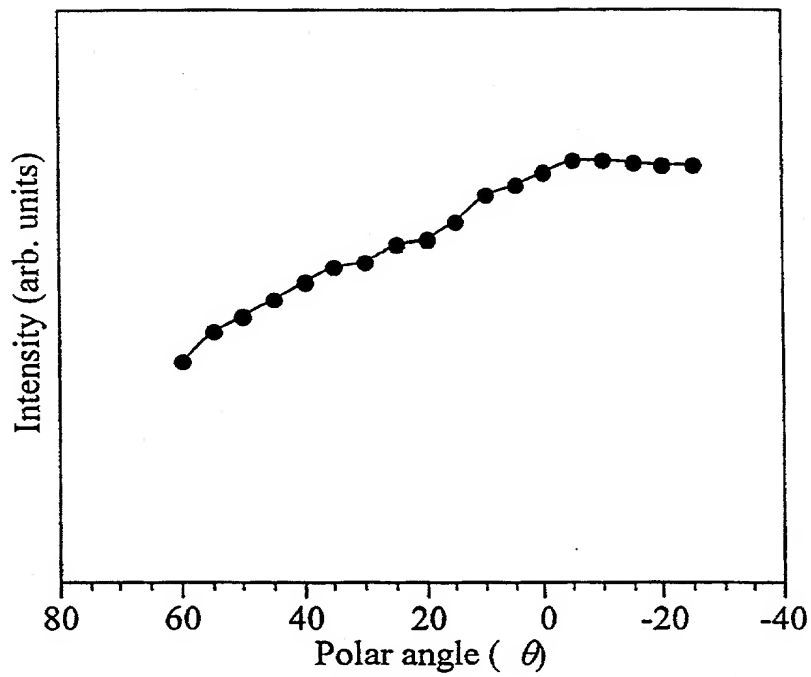
Zn3p
Zn3d
ZnLMM
1000
800
600
400
200
0
Binding energy
(eV)

Figure 4



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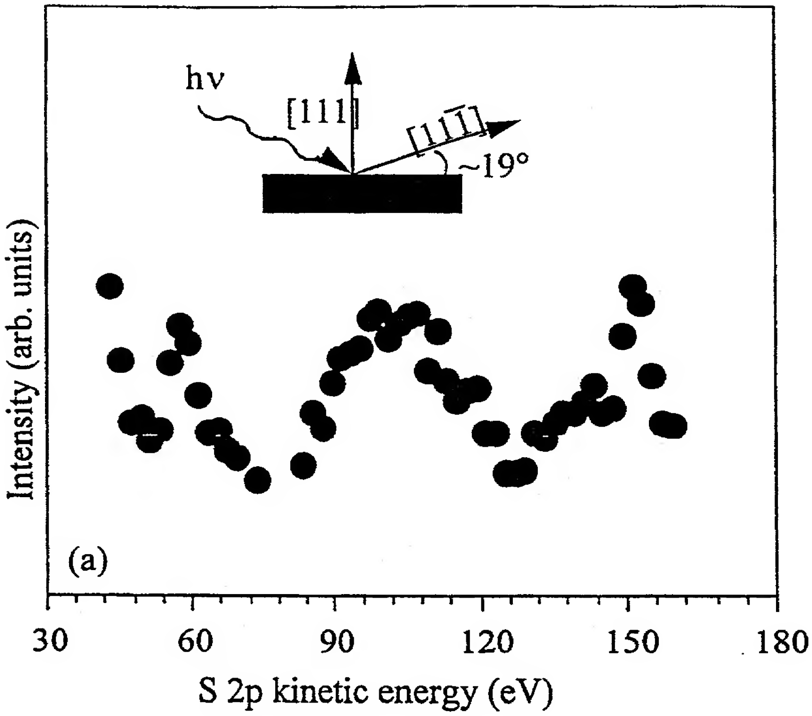

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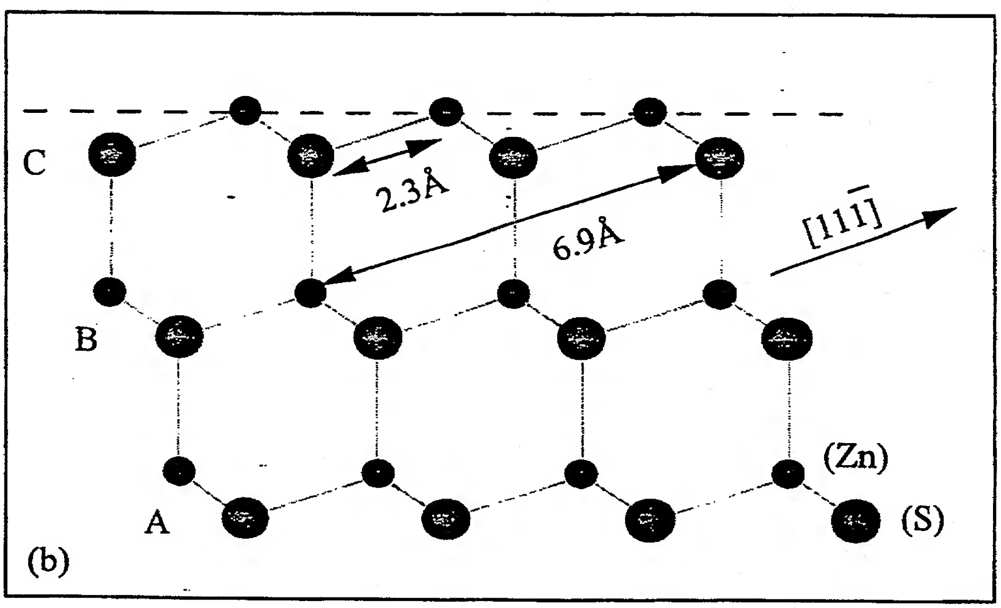

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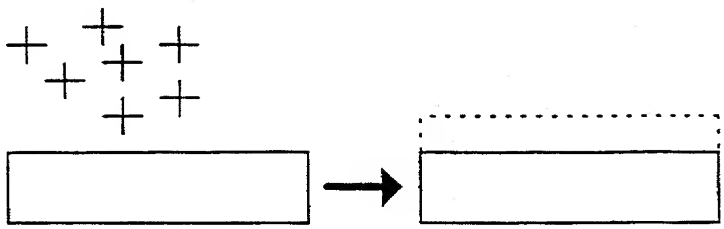

Figure 8

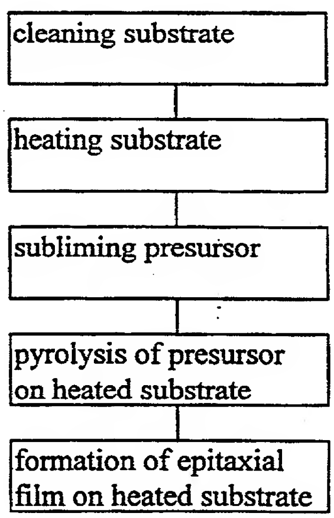

Figure 9

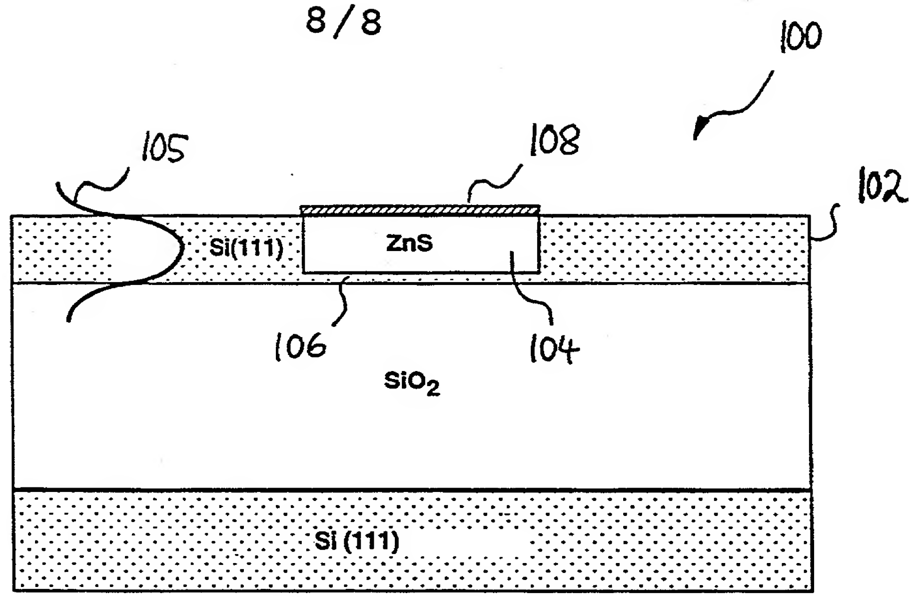

Figure 10

99/417/US

Customized PTO/SB/01 (10-01)

DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION	Docket No.	P07472US00/WEJ
	1st Inventor	TRAN, Nguyen H.
		COMPLETE IF KNOWN
____ Declaration Submitted **with** Initial Filing	Serial No.	10/018,401
x Declaration Submitted **after** Initial Filing	Filing Date	19 December 2001

As a below named inventor, I hereby declare that:
My residence, mailing address and citizenship are as stated below next to my name.
I believe I am the original and first inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

the specification of which:
____ is attached hereto
OR
X was filed on 20 June 2000 as PCT International Application No. PCT/AU00/00696, and (if applicable) was amended on .

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment specifically referred to above.
I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim FOREIGN PRIORITY benefits under 35 USC 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, inventor's certificate(s), or 365(a) of any PCT internat'l application which designated at least one country other than the US, listed below and have also identified below by checking the box, any foreign application for patent, inventor's certificate(s), or any PCT internat'l application having a filing date before that of the application on which priority is claimed. (___ *ADDITIONAL APPLICATIONS IDENTIFIED ON ADDITIONAL INFORMATION SHEET*)

Prior Foreign Appl. No.	Country	Day/Month/Year Filed	Priority Not Claimed
PQ1121	AU	22 JUNE 1999	

As a named inventor, I hereby appoint the registered practitioners of **LARSON & TAYLOR, PLC** associated with **Customer Number 000881** to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith. Direct all correspondence to that Customer Number.

Direct all telephone calls to WILLIAM E. JACKSON ,
at TEL (703) 739-4900 (Fax: 703-739-9577) e-mail:

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 USC 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon. (___ *ADDITIONAL INVENTORS IDENTIFIED ON ADDITIONAL INFORMATION SHEET*)

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